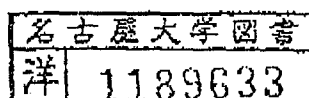


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John S. Rigden

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citation energy of the collective motion of the interacting atoms vibrating about their equilibrium positions.

The phonons have definite energies, given by the product of Planck's constant times their respective frequencies. Since phonons also correspond, respectively, to definite wavelengths, they also possess definite wave numbers that define wave vectors once the direction of wave propagation is specified. The phonons' wave vectors play the role of quasi-momentum vectors when multiplied by Planck's constant divided by 2π . The definite phonon quasi-momenta and their corresponding energies that span a spectrum form the basis for a particle-like description of these phonon excitations that make up the vibrational energy levels of the crystalline lattice.

The particle-like properties of the phonon excitations readily lend themselves to explanations of the thermodynamic properties of solids, and also the solid's capacities to conduct heat and electricity. The contribution to the heat capacity of a crystalline solid from the lattice vibrations can be viewed as arising from the thermal excitation of particle-like phonons of different energies. Since lattice imperfections will always be present in a crystal to some extent, the propagation of phonons may be interrupted and they can then be scattered either with some loss of energy or alteration in direction of propagation, or both. Such scattering of phonons as they travel from a hotter region of the crystal, where they are more numerous, to a cooler region, where fewer are excited, serves to limit the rate of transport of phonon energy and therefore the thermal conductivity of the lattice. In a crystal that contains conduction electrons, the phonons may scatter the electrons and limit the ability of an applied electric field to cause the conduction of electricity.

See also: CONDENSED MATTER PHYSICS; OSCILLATOR, HARMONIC

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MICHAEL J. HARRISON

PHOSPHORESCENCE

Some materials luminesce—that is, emit light—when they are subjected to an exciting source (photons, electrons, etc.). If the material continues to luminesce after the exciting source is removed, it is exhibiting either phosphorescence or fluorescence. If the time it takes the "afterglow" to dim depends on the temperature of the material, the material is phosphorescent. In general, the decay time decreases with increasing temperature. If the afterglow decay time is independent of temperature, the material is fluorescent.

Fluorescence and phosphorescence are quantum effects. An atom that is excited by a photon into an elevated energy state may decay to the lower state via some intermediate state (see Fig. 1). The photons emitted in this decay will have an energy lower than that of the incident photon.

Another significant difference between phosphorescence and fluorescence is their respective decay times. An excited atom in a fluorescent material decays to its ground state in about 10^{-8} second, whereas an excited atom of a phosphorescent material may remain in an excited metastable state for several hours.

A common mechanism of phosphorescence occurs when electrons or holes are set free by the excitation and trapped by lattice defects. The electrons or holes are then released from these traps by thermal vibrations in the lattice and recombine with oppositely charged carriers and emit a photon. The intermediate state shown in Fig. 1 represents the state of the system with the electron or hole trapped.

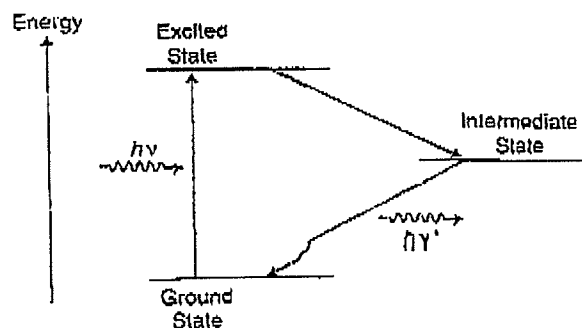


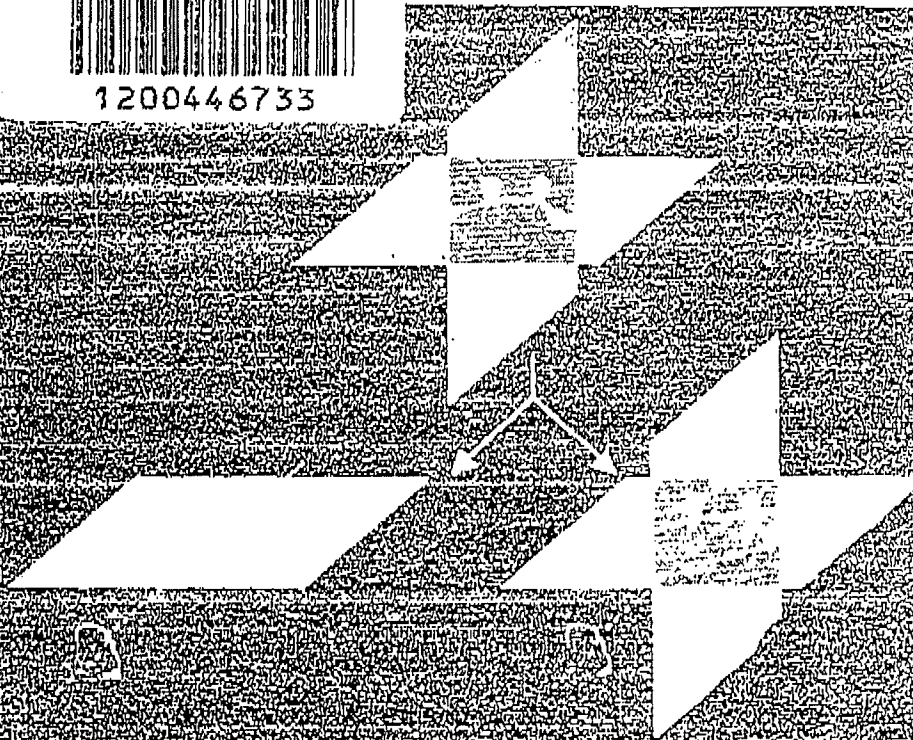
Figure 1

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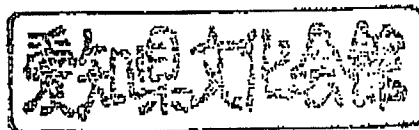
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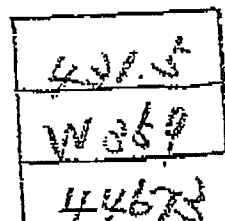
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Emission processes (1)

4.1 Luminescence

The emission of radiation from excited species is one of the several paths by which the excess energy may be lost (path vi, Fig. 1.1); the general phenomenon of light emission from electronically excited species is known as *luminescence*. In this chapter and the next we shall discuss luminescent processes. First, simple luminescent phenomena are considered, and then, in Chapter 5, *sensitized luminescence* is described: the latter process involves *intermolecular* energy transfer (path iv, Fig. 1.1) and electronic excitation is produced in a species other than the one that was initially excited. *Intramolecular* energy transfer, which populates a different *state* of the same *species*, is discussed in the present chapter.

Luminescent emission provides some of the most reliable information about the nature of primary photochemical processes. Competition exists between emission and other fates of excited species (quenching, reaction, decomposition, etc.), and the dependence of emission intensity on temperature, reactant concentrations, etc., may yield valuable data about the nature and efficiencies of the various processes. In particular, quenching by bimolecular collisions, and unimolecular energy degradation by radiationless transitions, are almost always best studied in terms of their effect on the intensity of luminescence. As well as possessing this fundamental interest, luminescent phenomena are also of considerable importance in several commercial and scientific applications, and an example will be given in Section 8.11.

The various individual luminescent phenomena are named according to the mode of excitation of the energy-rich species. We are concerned primarily with excitation by absorption of radiation, and emission from species excited in this way is referred to as *fluorescence* or *phosphorescence*: the distinction between the two processes is discussed below. Emission following excitation by chemical reaction (of neutral or charged species) is known as *chemiluminescence*, and is described briefly in Section 4.7. Other means of providing electronic excitation, which will not be discussed further, are by heat (e.g. in NO_2 —*pyroluminescence*), by an electric field (e.g. in solid ZnS —*electroluminescence*), by electron impact in gases (e.g. in discharge lamps), by

electron impact on solid phosphors (e.g. in television tubes—*cathodoluminescence*), by crushing crystals (e.g. uranyl nitrate—*triboluminescence*), and by rapid crystallization from solution (e.g. strontium bromate—*crystallo-luminescence*). Although we shall have occasion to refer to the luminescence of substances trapped in rigid glasses, we shall omit general discussion of the luminescence of solids. The emission of radiation from solids, especially inorganic compounds, is a complex phenomenon, but of the greatest importance (e.g. colour television requires inorganic phosphors possessing emissions of specific colours and intensities). For an introduction to such luminescence, the reader is referred to Chapter 5 of *Luminescence in chemistry* (Bibliography).

The two emission processes in which the ultimate source of excitation is absorption of radiation—fluorescence and phosphorescence—were originally distinguished in terms of whether or not there was an observable 'afterglow'. That is, if emission of radiation continued after the exciting radiation was shut off, the emitting species was said to be phosphorescent, while if emission appeared to cease immediately, then the phenomenon was one of fluorescence. The essential problem is what is meant by 'immediately' in this context, since the observation of an afterglow will obviously depend not only on the actual rate of decay of the emission (see Section 4.2 for further discussion of emission lifetimes), but also on the techniques used to observe it. Various instruments were devised to observe 'short-lived' luminescence, and in the early 1930s a luminescence with a lifetime of less than about 10^{-4} s was thought to be short-lived and, hence, fluorescent. In 1935 Jablonski interpreted phosphorescence as being emission from some long-lived metastable electronic state lying lower in energy than the state populated by absorption of radiation (cf. Section 3.5). Several workers (among them Lewis and Kasha, and Terenin) suggested that the long-lived metastable state was, in fact, a triplet state of the species, and as we shall see in Section 4.4, there is now considerable experimental evidence to substantiate this hypothesis. The long lifetime of the emission is a direct consequence of the 'forbidden' nature of a transition from an excited triplet to the ground-state singlet; that electric dipole transitions occur at all where $\Delta S \neq 0$ is due to the inadequacy of S to describe a system in which there is spin-orbit coupling (cf. Section 2.6). Extension of this idea to other systems, not necessarily triplet-singlet, in which $\Delta S \neq 0$ leads to the useful definition of phosphorescence as a *radiative transition between states of different multiplicities*: fluorescence is then understood to be a radiative transition between states of the *same* multiplicity. Figure 4.1 is a Jablonski diagram (see pp. 45–47 and Fig. 3.5) showing the processes of fluorescence and phosphorescence. These definitions are used almost universally by organic photochemists, although they might be extended to include within the scope of phosphorescence emission processes involving a transition forbidden by any selection rule rather than just the

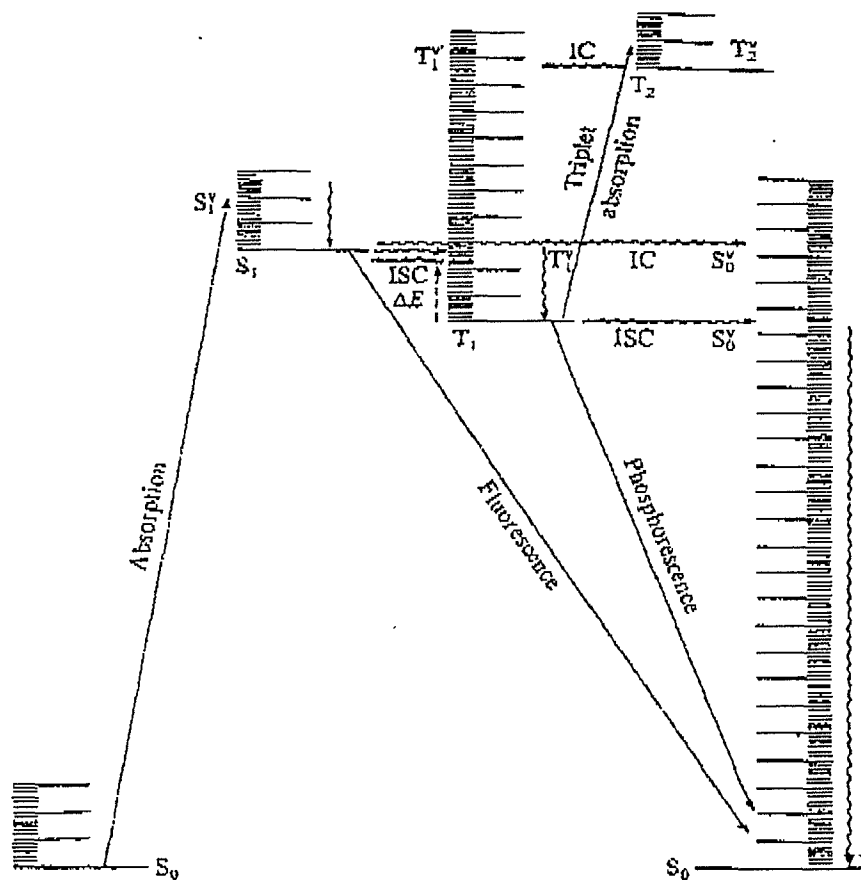


Fig. 4.1 Jablonski diagram showing absorption, and the emission processes of fluorescence and phosphorescence.

$\Delta S = 0$ rule. Since the distinctions between allowed and forbidden transitions are not sharp, the definitions lack some precision.

Absorption of radiation in a singlet-triplet transition is weak, since it is forbidden in the same way as the triplet-singlet phosphorescent emission. It follows that phosphorescence can only be excited inefficiently by direct absorption of radiation, and phosphorescence is much more usually the result of emission from a triplet populated by intersystem crossing from an excited singlet formed on absorption. The sequence of events is illustrated in Fig. 4.1. Absorption populates S_1^* ; vibrational energy, at least in condensed phases, is rapidly degraded and S_1^* can then lose its energy by radiation, intersystem crossing (ISC) to T_1 , or internal conversion (IC) to S_0 . It is, perhaps, surprising that ISC to T_1 , which is spin-forbidden by a radiationless

transition selection rule, can compete effectively with spin-allowed fluorescence and IC to S_0 ; phosphorescence is, however, observed in many systems, suggesting that IC from $S_1 \rightarrow S_0$ is relatively inefficient. A complete understanding of the photochemistry of a molecule really requires that the efficiencies (i.e. quantum yields) be known for all the processes occurring. Even if chemical reaction, decomposition, and physical quenching of an excited species do not occur, it is still necessary to measure quantum yields for fluorescence (ϕ_f), phosphorescence (ϕ_p), intersystem crossing $T_1 \rightarrow S_0$ (ϕ_{isc}) and internal conversion $S_1 \rightarrow S_0$ (ϕ_{ic}). With the restrictions on the processes occurring, it follows that

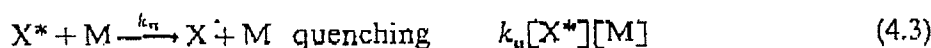
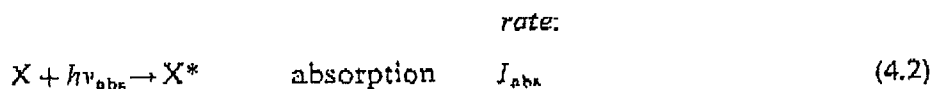
$$\phi_f + \phi_p + \phi_{isc} + \phi_{ic} = 1 \quad (4.1)$$

(although the relative magnitudes of the four quantum yields may be affected by the external environment).

4.2 Kinetics and quantum efficiencies of emission processes

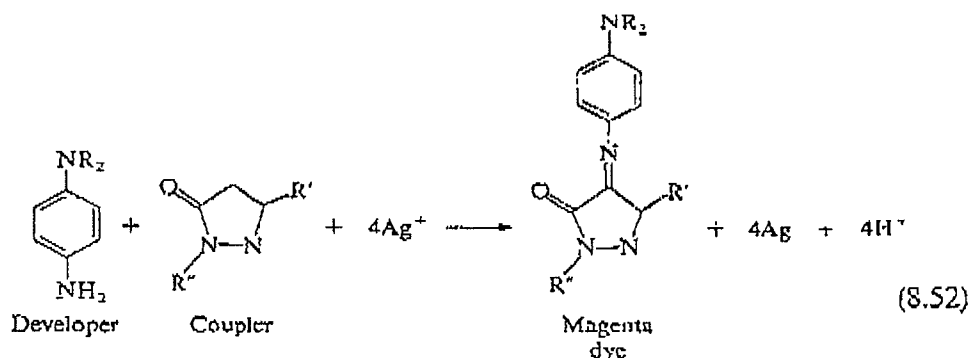
Considerable information about the efficiencies of radiative and radiationless processes can be obtained from a study of the kinetic dependence of emission intensity (or quantum yield) on concentrations of emitting and quenching species. In this section we shall consider first the application of stationary-state methods to fluorescence (or phosphorescence) quenching, and then discuss the lifetimes of luminescent emission under non-stationary conditions.

Observable effects in the quenching of fluorescence are usually the result of competition between radiation and bimolecular collisional deactivation of electronic energy, since vibrational relaxation is normally so rapid, especially in condensed phases, that emission derives almost entirely from the ground vibrational level of the upper electronic state: this point is discussed further in the next section. The simplest excitation-deactivation scheme, which does not allow for intramolecular radiationless processes, is



Solution of the steady-state equations for $[X^*]$ (i.e. with $d[X^*]/dt=0$) leads to the result that

$$I_{emitted} = A[X^*] = \frac{AI_{abs}}{A + k_q[M]} \quad (4.5)$$



We note that since the silver image formation is a negative process (dark areas produced by exposure to light), it is also necessary to arrange for the 'negative' or subtractive colours to appear on development. The magenta image formed in reaction (8.52) is a response to exposure to green light; similarly, a cyan dye is produced by red light, and a yellow one by blue light. A second negative colour process, such as printing on paper, then yields a positive reproduction of the original subject with the correct colours.

8.7 Photochromism

Silver halide photography involves the production of an essentially permanent optical effect by means of an irreversible photochemical process. The production of a *reversible* photoinduced colour change is referred to as *photochromism*. In photochromic systems, irradiation drastically alters the absorption spectrum; but when the irradiation source is removed, the system reverts to its original state. In some cases the reversal can be brought about by light of a different wavelength. The visible effect often involves the appearance of colour in a previously colourless material, although changes in colour—for example from red to green—are also known.

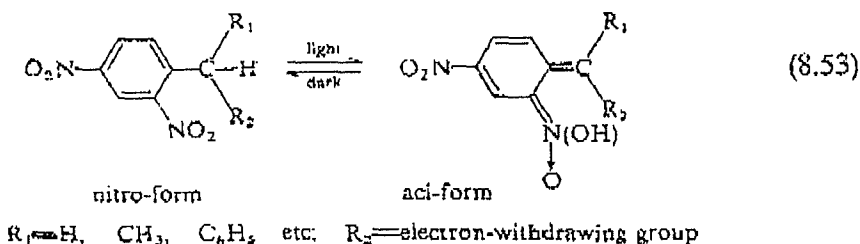
Numerous applications of photochromic substances have been suggested, and some of these have entered commercial practice. Photochromic sunglasses and spectacles are familiar, and plastics incorporating a photochromic dye have also been used for aircraft windows that darken in bright sunlight but become lighter again under less intense illumination. Various kinds of data storage are possible, including image storage for uses like those of photography. Very high resolution is possible, and the immediate appearance of the image on exposure, without further treatment, is a potentially great advantage over other processes. A rather more frivolous application is in the manufacture of toy dolls that can be 'suntanned': a photochromic dye is used that produces a brown coloration on exposure to sunlight.

The major difficulty in the use of materials incorporating photochromic materials is the rapid 'fatigue' exhibited by most known photochromic

substances. Many of the photochromic systems reported are really able to undergo reversal only a limited number of times. Photochromism based on isomerization (see below) offers the best prospect of good fatigue characteristics, since, with alternative systems that involve bond cleavage, a very small lack of reversibility soon leads to chemical decomposition in side-reactions.

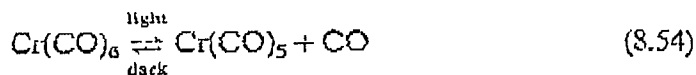
The main mechanisms responsible for photochromic behaviour are isomerization, dissociation, and charge-transfer or redox reactions. Many hundreds of specific photochromic substances are known, and a few examples must suffice to illustrate how photochromism arises.

Many aromatic nitro-compounds exhibit photochromic isomerization: the process is believed to involve photoisomerization from the colourless nitro-form to the coloured aci-form:

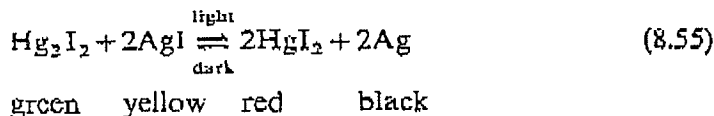


(The aci-form must also undergo some dissociation, since it is a strong acid.)

Irradiation of chromium hexacarbonyl in a plastic matrix (ca. 0.1% $\text{Cr}(\text{CO})_6$) leads to the formation of a deep yellow colour as a result of photodissociation of the hexacarbonyl. In the plastic, CO cannot escape, and recombination occurs in about 4 h at room temperature:



Both organic and inorganic charge-transfer or redox photochromic systems are known. A typical reversible photochemical redox reaction occurs in a mixture of mercurous iodide and silver iodide:



Heterolytic bond dissociation is responsible for photochromism exhibited by a large number of spiropyran derivatives

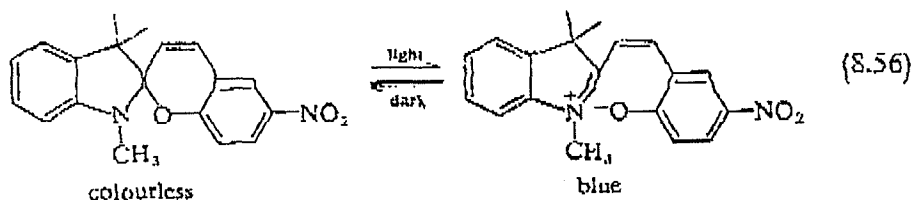


Fig.1

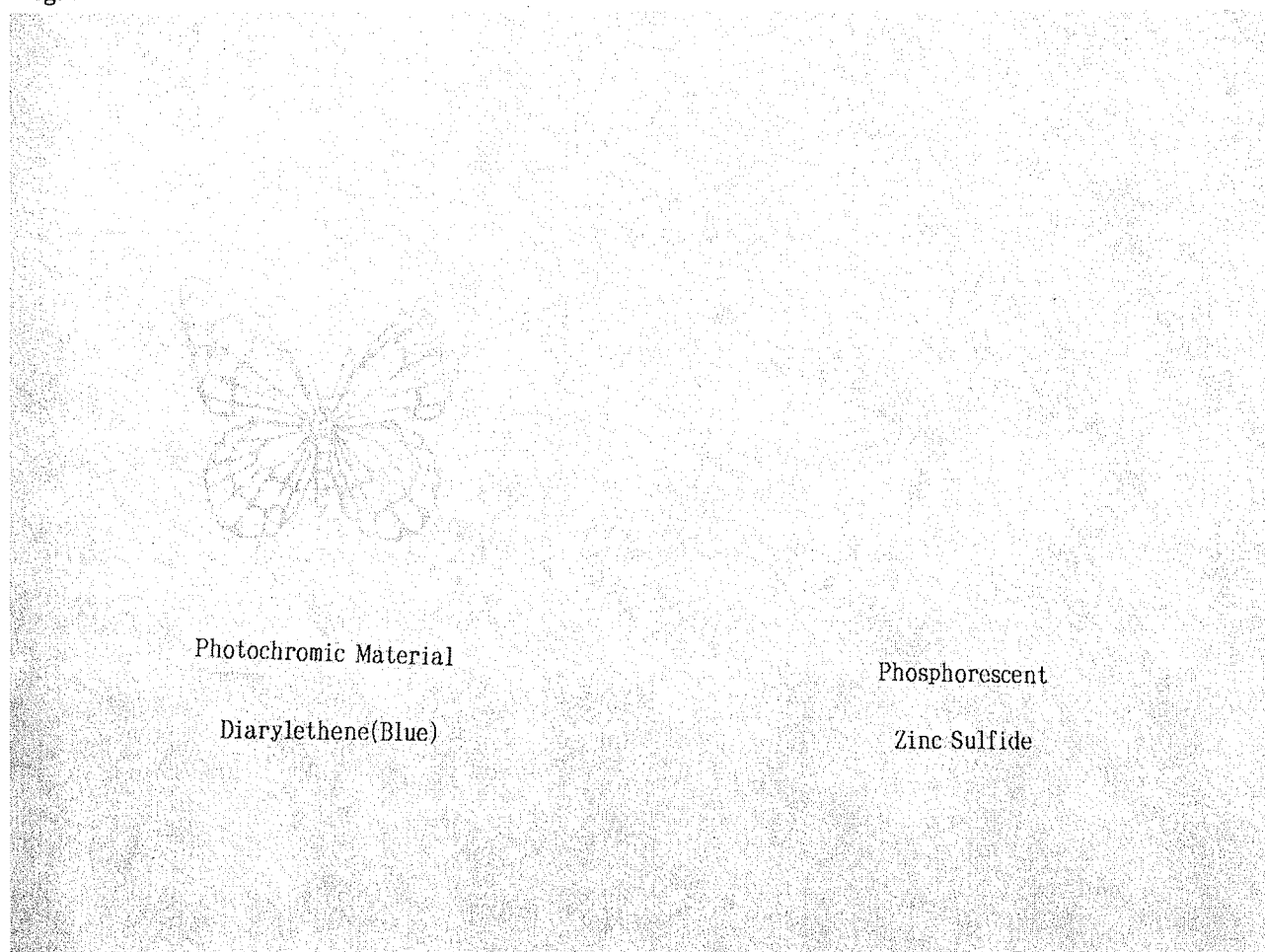


Fig.2

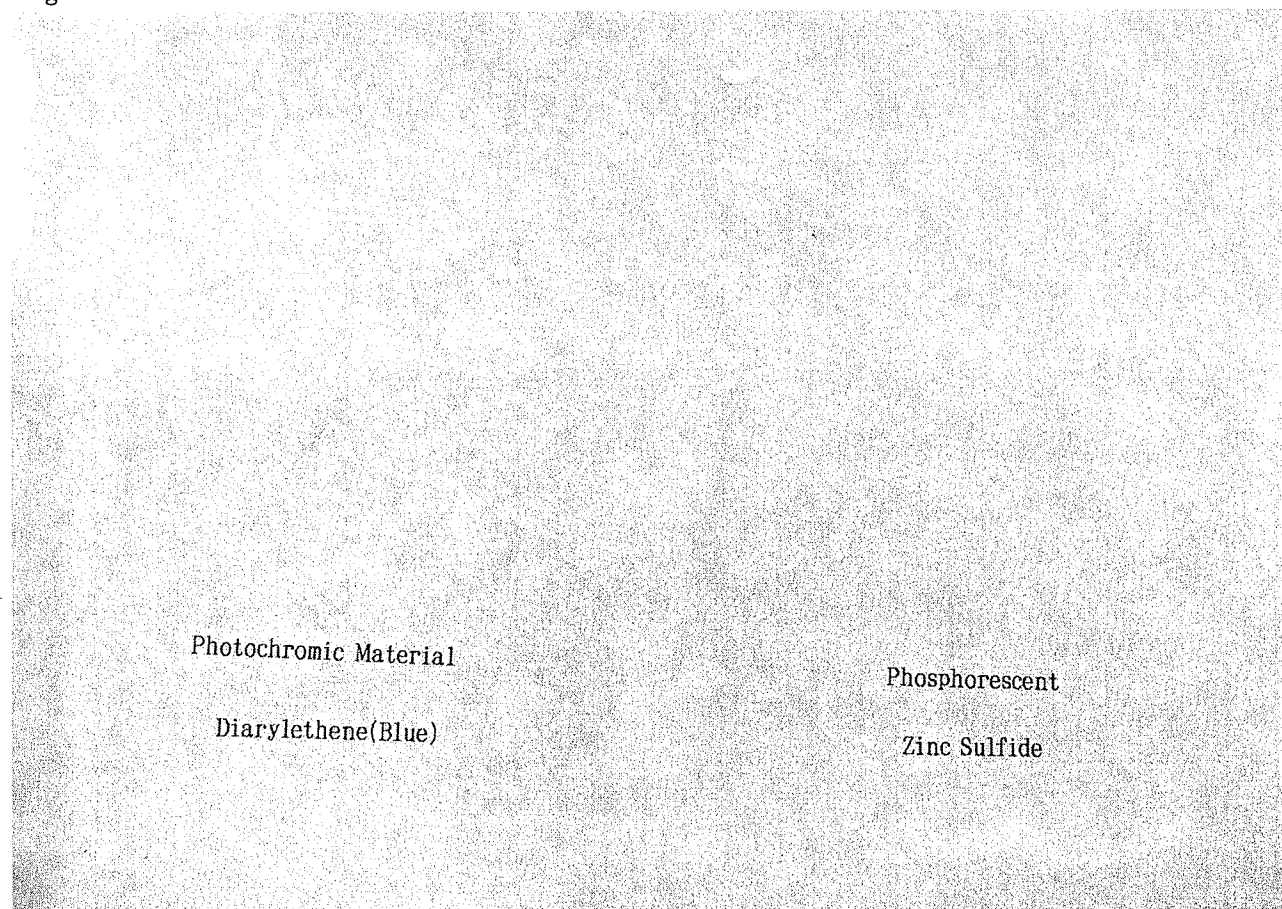


Fig.3

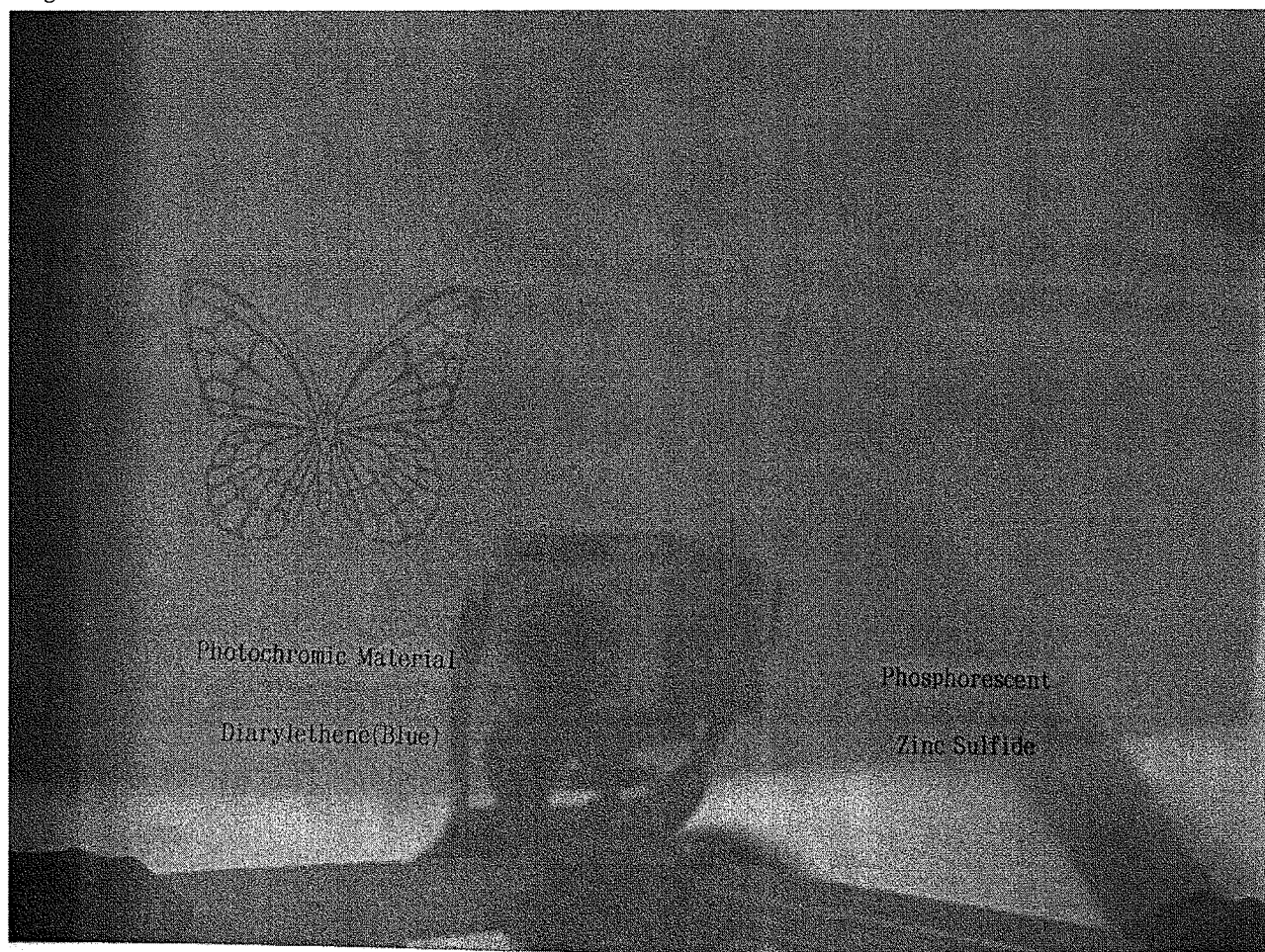


Fig.4

